(54) IMPROVEMENTS IN AND RELATING TO METHODS OF MANUFACTURING SINGLE CRYSTALS OF SEMICONDUCTOR MATERIAL

(71) We, PHILIPS ELECTRONIC AND ASSOCIATED INDUSTRIES LIMITED, of Abacus House, 33 Gutter Lane, London, E.C.2, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a method of manufacturing rod-shaped, dislocation-free single crystals of silicon. It furthermore relates to a single crystal manufactured by this method and also to semiconductor devices, in particular photosensitive targets, comprising a portion of such a single crystal.

In manufacturing single crystals from meltable semiconductor material by solidification in substantially one direction, it is not only endeavoured to obtain the lowest possible concentration of undesirable impurities which can influence the semiconductor properties of the crystal, but also to produce a high crystal perfection, i.e. having as few deviations from a perfect ordering of the atoms in the crystal as possible.

As regards the impurity elements, in particular those elements are of influence which in the semiconductor material act as a donor or acceptor or as a recombination centre. However, there are also elements which were deemed to have generally little influence on the conduction properties of semiconductor material.

As regards disturbances in the structure of the crystal lattice in a semiconductor single crystal, attention was paid in particular to the so-called dislocations. Dislocations are disturbances in the crystal lattice which continue substantially linearly in the crystal. They may grow further in the material crystallizing from the melt. They may grow to the surface of the crystal and terminate there. In general they continue in a straight line but locally their direction may vary comparatively abruptly.

Undesirable impurities may accumulate along such dislocations as a result of which the electric properties of the crystal are varied locally. When, for example, such a dislocation intersects a p—n junction, an increased leakage current or possibly a decreased breakdown voltage may occur locally.

Furthermore it is often desirable in manufacturing semiconductor devices to etch a semiconductor surface so as to be accurately plane. With some slow etchants, the presence of dislocations may give rise to an etching which is locally accelerated, so-called etch pits being formed. Methods of making dislocations visible at the surface are based on the latter phenomenon.

For that purpose there are used anisotropic etchants, i.e. etchants which preferentially etch more slowly according to certain crystallographic directions than in directions with other crystallographic orientation.

In the interior of the semiconductor crystal, for example of silicon or germanium, the above-mentioned property of dislocations to induce accumulations of certain impurities may be used for demonstrating dislocations. By using a metal which diffuses at a comparatively low temperature and which collects strongly along dislocations, for example copper in germanium or silicon, the dislocations may be made visible by means of infrared radiation having a wavelength above the absorption limit of the semiconductor material. Dislocations may also be made visible with X-ray radiation without it being required to introduce a special impurity. This method is based on deviating X-ray diffraction with local disturbances in the crystal lattice.

Methods have become known for manufacturing fully dislocation-free crystals. For this purpose thermal conditions have already been considered, for example in drawing a crystal or in floating zone-melting, so that substantially no radial temperature gradient in directions transverse to the direction of growing of the rod-shaped crystal is present, for example, by compensating for

lateral radiation. A very gradual cooling has further been considered. It has been found, however, that dislocations already present can go on growing in these circumstances. The starting crystal may be a dislocation-free seed crystal but the strong temperature variations which occur when the seed crystal is contacted with the melt may generate such large mechanical stresses that dislocations are formed. Melting away of the part of the seed crystal in which said dislocations are formed generally is not sufficient to obtain a dislocation-free starting material since said new dislocations start growing in the adjacent parts of the seed crystal which are heated during said melting away. Upon crystallization after said melting away, said dislocations can continue to grow in the growing crystal material. In principle, however, it is possible to prevent the formation of such dislocations by careful preheating.

It has furthermore been found that once the crystal material in the growing part is dislocation-free, the formation of new dislocations in the growing material can easily be prevented without choosing very critical growth conditions. Methods are known to restrict the growth of dislocations present or formed in the seed crystal in such manner that ultimately a dislocation-free growth is obtained after which the conditions of growth can be varied more freely without inducing new dislocations. For that purpose the seed crystal is allowed to grow with a small diameter as a result of which existing or formed dislocations obtain a better chance to laterally reach the crystal surface, their continuation in the longitudinal direction of the growing crystal being discontinued. When in the thin-growing part of the crystal, the dislocations have disappeared, growth may be effected with gradually increasing diameters without new dislocations being formed.

In addition to the above mentioned dislocations which continue substantially linearly in a crystal, disturbances in the regular lattice structure of the atoms in a crystal may be of a different nature. For example, an atom may be lacking locally in the crystal lattice. Such a lattice defect is referred to as a "vacancy". The equilibrium concentration of such vacancies in a crystal lattice, determined thermodynamically, is to some extent comparable to the solubility of a foreign atom. This may be referred to as maximum solubility of vacancies at a given temperature. The solubility is considerable at high temperatures and decreases at lower temperatures. Furthermore, in principle, vacancies can move through the crystal, which may be referred to as diffusion phenomena, as in the case of diffusion of foreign atoms. It will be obvious that these diffusion phenomena are also temperature dependent and it is to be expected that the diffusion rate will decrease when the temperature decreases. The influence of vacancies on the conductivity properties of semiconductor single crystals may be quite different from the influence of foreign atoms. The direct influence of scattered individual vacancies in the crystal lattice on the electric properties has hardly appeared in crystals of elementary semiconductors such as germanium or silicon. It has been found that accumulations of impurities, for example copper in silicon or germanium, can occur not only at the area of dislocations, but also in more arbitrarily spread places in the crystal lattice, in particular in a crystal or part of a crystal which is free from dislocations. Such accumulations were ascribed to the presence of accumulations of vacancies, so-called "vacancy-clusters". These vacancy-clusters were the cause that in a preferential etching treatment etch-pits were formed in a surface of a dislocation-free crystal, which pits were visible with an optical microscope. These vacancy-clusters were believed to be formed during the crystallisation since when the temperature falls the solubility of vacancies would decrease so strongly that said vacancies precipitate locally in the crystal. Many of said vacancy-clusters were found in particular when manufacturing dislocation-free silicon crystals, in which a very thin part was first grown on the seed crystal. In order to grow said thin part, drawing speeds were actually used at which the crystallized material cooled rapidly. It has therefore been indicated that in growing further dislocation-free material the concentration of such vacancy-clusters could be decreased by low rates of growth, if desirable associated with a suitable afterheating, since the vacancies then can diffuse to the surface in time when the solubility decreases due to said gradual cooling.

It has now been found that such vacancy-clusters in the crystal may have similar drawbacks as dislocations. It has been found, for example, that in a silicon target having a mosaic of planar diodes on a dislocation-free silicon crystal, diodes having too high a leakage current are still present locally. If during operation of such a target in a camera tube the signal therefrom is converted in a display tube into a picture, a number of scattered white dots in a black field become visible in the picture formed with the display tube when the target in the display camera tube is not exposed, which white dots correspond to the location of the diodes having high leakage currents in the silicon target. The topography of said white dots is analogous to the topography of etch-pits in a surface of dislocation-free silicon crystals obtained by means

of an anisotropic etching treatment using an etchant which manifests dislocations.

It is the object of the invention to provide a method of manufacturing dislocation-free semiconductor single crystals by growing from a melt in substantially one direction, in which the formation of such centres in the crystal, referred to above as "vacancy-clusters", is counteracted and in particular dislocation-free and vacancy-cluster-free crystals are obtained. "Vacancy-cluster-free" is to be understood to mean herein the absence of clusters which can be made visible by means of an anisotropic etching treatment (using an etchant which is used to manifest dislocations) but does not exclude the presence of vacancy-clusters which are too small to be made visible by anisotropic etching.

The following recognitions have led to the present invention. Vacancies as such will presumably not unite to vacancy-clusters so rapidly without nuclei being present locally which tend to bind the vacancies. It is likely that vacancies can have a high mobility. It was stated earlier, for example, that the migration energy of punctiform defects in a silicon lattice may be extremely low, namely approximately 0.2—0.3 eV. This would mean that even at room temperature such vacancies in silicon are still movable. It may therefore be assumed that also in the case of a comparatively rapid cooling the decrease in concentration can be effected sufficiently rapidly by migration of the vacancies to the crystal surface.

It is assumed that upon forming centres for attracting vacancies to vacancy-clusters, foreign atoms would play a part. The vacancy clusters, however, also occur when the starting material and the crystallization process fulfil very high requirements as to purity. Even when silicon purified to a high degree by floating zone melting, is chosen as the starting material and the crystallization process is also carried out by floating zone melting in a very pure atmosphere, for example, argon of a high purity, while in addition the occurrence of dislocations is counteracted, then the above-mentioned vacancy-clusters are still found. It is furthermore assumed that during the formation of the nuclei for vacancy-clusters oxygen plays an important part. Oxygen belongs to those impurities which were deemed to be generally of little influence on the conductivity properties of the semiconductor material, in particular germanium and silicon, and the presence of which in the semiconductor material is hard to establish. The possibility of pollution of the semiconductor material by oxygen is large, however, in view of the many possibilities of introduction of oxygen from the atmosphere or from oxygen-containing material in

the apparatus used, for example, a quartz crucible, and moreover the semiconductor material may have a large affinity for oxygen. A high content of oxygen, however, has turned out to influence the properties of a semiconductor crystal. It had been found, for example, that with an oxygen concentration of approximately 10^{18} atoms per cu.cm in silicon, the conductivity properties may change after thermal treatments. The oxygen content was determined by means of the infrared absorption band in silicon at a wavelength of 9 μm which is ascribed to silicon oxygen bonds in the crystal. It was known to maintain the oxygen content in a silicon single crystal so low that the oxygen could no longer be detected by means of the 9 μm absorption band. This was the case when it was ensured that crystallization was carried out in an oxygen-free atmosphere and the melt was kept out of contact with an oxygen-containing wall, for example a quartz wall. Similar crystals were obtained with zone melting without the use of a crucible in a vacuum, in oxygen-free argon or in hydrogen. A better oxygen-eliminating effect of one of the said atmospheres above any of the others was not established. What was established was that hydrogen is soluble to such a strong extent in molten silicon with a much smaller solubility in solid silicon, that, in the case of rapid crystallization, cavities could be formed in the silicon crystal which were visible by means of an infrared camera.

Nevertheless it has been found that vacancy-clusters occur in material in which oxygen can no longer be detected by means of the above described infrared absorption method, but this method is not so accurate that concentrations below approximately 5×10^{16} oxygen atoms per cu.cm in monocrystalline silicon can be detected as such. It is assumed that the nuclei where the vacancies could unite to form vacancy-clusters, consist of complexes of vacancies and oxygen, for example one vacancy having n atoms of oxygen, where n exceeds 2. The invention is furthermore based on the recognition of the fact that such a complex is stable only below a given temperature, probably also dependent upon the number of oxygen atoms per complex.

The invention is furthermore based on the consideration that the probability for the formation of such complexes can be reduced by using a reaction between oxygen and another impurity which enters into competition with the reaction for the above-mentioned complex-formation and reduces the number of oxygen atoms which is available for forming the complexes. A further consideration which has resulted in the method according to the invention is that

the crystallized material should traverse, in a short period of time, the temperature range from the uppermost stability limit of the oxygen vacancy complexes down to the limit below which oxygen has no reasonable transit time in the semiconductor material so as to keep the probability that remaining unbound oxygen atoms would unite, low.

The present invention provides a method of manufacturing a single crystal of silicon having a rod-shaped, dislocation-free part with a diameter of at least 1 cm, the method comprising the step of solidifying molten silicon in substantially one growth direction in a substantially oxygen-free atmosphere, taking known measures to prevent formation of dislocations during the growth of the rod-shaped crystal part having a diameter of at least 1 cm, additionally growing the crystal in a hydrogen-containing atmosphere in combination with a rate of displacement of the part of the crystal having a diameter of at least 1 cm relative to the melt of more than 2 mm per minute so that the formation of vacancy oxygen complexes which serve as nucleation centra in the formation of vacancy clusters is counteracted in such manner that the growing rod-shaped, dislocation-free part of the crystal is vacancy-cluster-free as hereinbefore defined. The hydrogen and the vacancies may be sufficiently mobile to diffuse out of the crystal to such an extent that the formation of clusters of hydrogen atoms, if desirable also formed by means of the vacancies, need not be feared.

Preferably the rate of displacement is at least 2.5 mm per minute, but in practice is preferably not higher than 15 mm per minute. For the hydrogen in the atmosphere used is preferably chosen a (partial) pressure of at least 0.02 atmosphere. In practice a gas atmosphere is preferably used the (partial) hydrogen pressure of between 0.05 and 0.3 atmosphere. It is to be noted that in order to obtain vacancy-cluster-free material a higher hydrogen pressure, for example atmospheric pressure, may also be used. As is known, the presence of much hydrogen, however, may result in strong convection currents in the atmosphere around the crystal, as a result of which a high surface cooling may occur with the danger of strong fluctuations in said cooling and an uneven solidification front, the danger existing of other undesirable phenomena, for example, a strong fluctuation in the concentrations of added desired dopants to obtain a given conductivity type and a given conductivity, and possibly even formation of dislocations. Measures may be used, for example radiation reflecting surfaces and/or after-heaters, to counteract too strong a radial temperature gradient and it is also possible to take measures which decelerate the gas circula-

tion, for example, in the form of screens in the current path of the gas flowing by convection. The gas which flows along the growing end of the crystal may also be pre-heated with these means or in another manner. The gas atmosphere may consist entirely of hydrogen but it is also possible to mix it with another gas, for example, a rare gas or another gas which does not react in the system. Preferably, sufficient quantities of this other gas are mixed to obtain a total gas pressure of approximately 1 atmosphere, so that, for example, a gas mixture of approximately atmospheric pressure is obtained which consists of a mixture of argon and hydrogen containing at least 5% by volume of hydrogen.

It is obvious that in carrying out the crystallization the introduction of oxygen should be counteracted as much as possible. When the method drawing crystals from a melt present in a crucible is used, it is of importance that the taking up of oxygen from the crucible wall should remain low. Preferably the crucible wall does not consist of oxidic material so as to avoid contact between such material and molten silicon with the melt is preferably avoided. Other crucible materials may give rise in the silicon, to the introduction of undesirable impurities. Therefore a crucible-free method, for example floating zone melting, is preferably used for the crystallization. For making the growth dislocation-free, the growth is first carried out preferably from the seed with a diameter smaller than 1 cm, for example, at most 5 mm, and a rate of growth of at least 10 mm per minute, after which the diameter of the crystal is increased. It is to be noted that said thin growth serves to restrict the growth of dislocations so that finally a dislocation-free growth is obtained. It is not necessary for this thin-grown part to be also vacancy-cluster-free. For convenience, hydrogen in the surrounding atmosphere may already be used in this stage of growth but this is not necessary. The hydrogen may be added afterwards, for example when growth starts with the desirable rod diameter.

In order that the invention may be readily carried into effect, it will now be described in greater detail, by way of example, with reference to the accompanying drawing, the sole figure of which is a diagrammatic side elevation of a stage in the manufacture of a silicon crystal by floating zone melting.

Reference numeral 1 in the figure denotes a rod-shaped body of polycrystalline silicon which is arranged vertically and is held at its lower end in a holder 2 which is connected, by means of a vertical shaft 12, to driving mechanisms (not shown) by means of which the rod 1 can be moved vertically and be rotated about its axis. The rod 1

has been purified by means of floating zone melting in which in particular in the last stage an oxygen-free argon atmosphere has been used. The rod 1 which constitutes the starting material for the manufacture of the silicon single crystal has a diameter of 25 mm and an original length of, for example, approximately 40 cm. A rod-shaped seed crystal 3 of silicon having a length of 5 cm and a diameter of 8 mm is secured to a holder 4 and is located above the rod 1 and coaxial therewith, said holder 4 being movable vertically by means of a vertical shaft 14 and rotatable about its axis by means of driving mechanisms not shown. The vertical and rotating movements of the holders 2 and 4 can be adjusted independently of each other. The assembly is arranged in a chamber 10 which is sealed from the atmosphere and in which a desired atmosphere can be adjusted by means of a gas inlet duct 11 and a gas outlet duct 13. The shafts 12 and 14 are movable in known manner and are passed in a gas-tight manner through the lower and upper ends (not shown) respectively, of the chamber 10. Inside the chamber 10 is furthermore provided a water-cooled high frequency coil 5 which can be supplied by a high frequency generator 15. The high frequency coil 5 consists of a single turn having an inside diameter of 30 mm and an outside diameter of 38 mm. The high frequency coil 5 is arranged horizontally and is coaxial with the rod 1 and the seed 3.

The following process is carried out for growing a monocrystalline silicon rod. The chamber 10 is first evacuated and gas of approximately atmospheric pressure is then passed through via the inlet and outlet 11 and 13, respectively. The gas consists of moisture-free and oxygen-free argon with 10% hydrogen purified by means of palladium. The gas is led through the chamber 10 at a rate of, for example, 1 litre per minute. It is to be noted that it is also possible after filling the chamber 10 with the gas mixture to close the inlet 11 and outlet 13. On the upper side of the rod 1 a silicon melt must be formed by high frequency induction. If desirable, after a known manner of heating to increase the conductivity of the silicon, the upper end of the rod 1 is placed in the field of the high frequency coil 5 in such a manner that at that region a molten zone is formed by inductive heating, which zone cannot flow down along the rod 1 due to the high surface tension of the molten silicon. The rod 1 is rotated about its axis, for example at a rate of 25 rpm.

The seed crystal 3 is now lowered gradually so that it is preheated partly by coupling-in of the high frequency field, partly by radiation from the molten zone. The preheated crystal 3 is then carefully contacted with the melt and the lower end of the seed crystal 3 melts. The seed crystal 3 is then drawn upwards at a rate of 15 mm per minute, a rod-shaped part 7 drawn from the melt 6 and having a diameter of 2—3 mm, growing on the seed crystal 3. Both during the downward movement of the seed crystal for dipping in the molten zone and subsequently during drawing, the seed crystal 3 is rotated about its axis at a rate of 30 rpm in a direction opposite to the rotation of the rod 1. During this whole drawing process the rod 1 is gradually moved upwards in such manner as to melt gradually so as to replenish in the molten zone 6 the material drawn from the melt. After the rod part 7 has obtained a length of approximately 5 cm, the rate of drawing and the supplied high frequency power are reduced, the diameter of the growing material being increased gradually. Dislocations, if any, growing from the seed crystal have been stopped in their growth by reaching the surface of the thin rod-shaped part 7. A further growth hence is dislocation-free.

As a result of the decrease in temperature of the melt and the reduction in drawing speed, in this case to 3 mm per minute, the diameter of the grown crystal is gradually increased so that a conical dislocation-free part 8 is formed. When a diameter of 23 mm has been obtained, the supply of the high frequency coil is readjusted in such manner that a rod-shaped part of constant diameter grows, the rate of drawing being maintained at 3 mm per minute. In this manner a rod-shaped part 9 of monocrystalline silicon is formed which can be processed in the usual manner by severing transverse to the axis of the rod to form slices which are suitable as starting material for the manufacture of semiconductor devices. Upon examination of the slices by etching of the surface with an anisotropic etchant it has been found that the manufactured rod-shaped single crystal 9 was both vacancy-cluster-free (as hereinbefore defined) and dislocation-free.

In a corresponding manner as described in the preceding example but with the use of an atmosphere which consisted only of pure argon and hence contained no hydrogen, dislocations were not found either in a rod-shaped part 9, as appeared from an X-ray examination, but the resulting slices were found to contain etch-pits upon etching with an anisotropic etching liquid which pointed to the presence of vacancy clusters in quantities which did not differ noteworthily from dislocation-free crystals obtained in the same gas and in corresponding circumstances but with the use of a drawing rate under 2 mm per minute.

In a corresponding manner as described

above with reference to the drawing but with the use of a drawing rate of 1 mm per minute for the growing of the thick rod-shaped crystal part, a crystal part 9 was obtained which was dislocation-free but which, as appeared from anisotropic etching examination of the resulting slices, was obviously not vacancy-cluster-free notwithstanding the presence of hydrogen in the atmosphere used during crystallization.

In a rod part 9 obtained in a corresponding manner at a rate of 2 mm per minute with the use of the hydrogen-containing atmosphere, vacancy-clusters of the type which could be demonstrated by anisotropic etching turned out to be present but in significantly much lower concentrations.

It is to be noted that, as is known, fluctuations in the crystallization rate may occur all the same when the drawing rate is kept constant, which fluctuations are the stronger according as fluctuations in the supplied current for the high frequency coil and/or deviations in the symmetry of the thermal conditions during crystallization are larger. It is obvious that, in the case of strong fluctuations of the crystallization rate, it is possible that also at drawing rates above 2 mm per minute vacancy-cluster-free material is not obtained locally. In particular, at drawing rates slightly higher than 2 mm per minute, there will be a chance of vacancy-clusters which can be demonstrated by anisotropic etching. Nevertheless, in the worst case a reasonable yield of cluster-free slices can be obtained all the same. In the growth conditions described which, as regards growth fluctuations, are subject to improvement, a crystal part 9 can be obtained with a drawing rate of 2.5 mm per minute which is cluster-free throughout its length.

It is to be noted that the term "vacancy-cluster-free" is to be understood to mean in the present case the absence of vacancy-clusters which can be by anisotropic etching. This does not mean that the presence of vacancy-clusters which are so small that they cannot be made visible by anisotropic etching, is excluded. It is to be expected, however, that the influence on the formation of etch-pits is more or less analogous to the influence on the electric and possibly other physical properties of the semiconductor material, i.e. that the influence on said properties of vacancy-clusters which can cause visible etch-pits will be large as compared with the influence hereon of the vacancy-clusters which cannot be detected by etching. Upon examining the above-mentioned dislocation-free and vacancy-cluster-free silicon with a more accurate detection method, the presence of very small vacancy-clusters can even be made observable locally in some cases. This method consists in the use of a low temperature diffusion of copper

and X-ray examination of the monocrystalline slices thus doped with copper. In the crystal part 9 obtained according to the example in which thus a drawing rate f 33 mm per minute was used, extremely small dots are found in some slices which point to vacancy clusters of a much smaller order of magnitude than the above-described vacancy-clusters which can be demonstrated by anisotropic etching. Rod parts have also been manufactured which contained none of the said very small vacancy-clusters while otherwise they were dislocation-free and vacancy-cluster-free.

It is to be noted that the influence of said very small vacancy-clusters on the electric and possibly other physical properties will be small relative to the clearly detectable vacancy-clusters. The explanation for the presence of the two types of vacancy-clusters could be as follows. The large vacancy-clusters are formed around nuclei consisting of one vacancy having a comparatively large quantity of oxygen atoms, for example 3 or more. The stability of the oxygen-vacancy complexes would be larger according as the complex comprises more oxygen atoms. Upon cooling newly crystallized dislocation-free material, first of all those oxygen-vacancy complexes will be formed which have the highest stability, since the crystal material, during cooling, first traverses a track in which complexes of vacancies having few oxygen atoms, for example 1 or 2 oxygen atoms, are not yet stable. It is possible that complexes of a vacancy having, for example, 1 to 2 oxygen atoms still occur at lower temperature but the earlier formed nuclei which have already grown to vacancy-clusters have a higher affinity to vacancies so that mainly these will grow further to large vacancy-clusters which may result in visible etch-pits upon anisotropic etching. Nuclei, if any, of a vacancy having little oxygen thus do not get the chance of growing to such an extent as to be visible with copper doping (also termed "copper decoration") and X-ray examination (in this case termed "X-ray topography").

Due to the presence of hydrogen and a sufficient cooling rate (resulting from a rate of displacement of the crystal relative to the melt of more than 2 mm per minute), the reduced quantities of oxygen atoms not bound by hydrogen, termed here free oxygen atoms, obtain an insufficient chance of forming complexes of a vacancy having much oxygen. It may be, however, that the remaining quantity of available oxygen at lower temperatures still has sufficient time and mobility of forming, for example, a complex of a vacancy having two oxygen atoms. The possibility of meeting is much larger. Since now complexes of a vacancy having

much oxygen are absent, the complexes with little oxygen obtain the chance of capturing more vacancies. As a result of the comparatively low temperature, at which the "small" nuclei (with little oxygen) have been formed, the number of available vacancies for forming vacancy-clusters has already been reduced so that said nuclei can grow only to small vacancy-clusters which cannot be made visible by anisotropic etching but can just be made visible by means of copper decoration and X-ray topography. When using hydrogen and a sufficiently high cooling rate, however, the formation of the complexes with few oxygen atoms is also suppressed.

WHAT WE CLAIM IS:—

1. A method of manufacturing a single crystal of silicon having a rod-shaped, dislocation-free part with a diameter of at least 1 cm, the method comprising the step of solidifying molten silicon in substantially one growth direction in a substantially oxygen-free atmosphere, taking known measures to prevent formation of dislocations during the growth of the rod-shaped crystal part saving a diameter of at least 1 cm, additionally growing the crystal in a hydrogen-containing atmosphere in combination with a rate of displacement of the part of the crystal having a diameter of at least 1 cm relative to the melt of more than 2 mm per minute so that the formation of vacancy-oxygen complexes which serve as nucleation centra in the formation of vacancy-clusters is counteracted so that the growing rod-shaped dislocation-free part of the crystal is vacancy-cluster-free as hereinbefore defined.

2. A method as claimed in claim 1, characterized in that the rate of displacement is at least 2.5 mm per minute.

3. A method as claimed in claim 1 or claim 2, characterized in that the rate of displacement is at most 15 mm per minute.

4. A method as claimed in any preceding claim, characterized in that the partial pressure of hydrogen is at least 0.02 atmosphere.

5. A method as claimed in claim 4, characterized in that the partial pressure of hydrogen is at least 0.05 atmosphere.

6. A method as claimed in claim 4 or claim 5, characterized in that the partial pressure of hydrogen is at most 0.3 atmosphere.

7. A method as claimed in any of claims 4 to 6, characterized in that the substantially oxygen-free atmosphere consists of a mixture of a rare gas and hydrogen containing at least 5% by volume of hydrogen and has a pressure of approximately one atmosphere.

8. A method as claimed in any preceding claim, using a floating zone melting process to grow the crystal.

9. A method as claimed in any preceding claim, characterized in that the starting material is a dislocation-free seed crystal.

10. A method as claimed in any preceding claim, wherein in that a first part of the crystal having a diameter smaller than 1 cm is grown on the seed crystal with a rate of displacement of the seed crystal relative to the melt of at least 10 mm per minute after which the diameter of the crystal is increased.

11. A method as claimed in claim 10, wherein the diameter of the first part of the crystal is not more than 5 mm.

12. A method of manufacturing a single crystal substantially as herein described with reference to the accompanying drawing, in which method the part of the crystal having a diameter of at least 1 cm is displaced relative to the melt at a rate of more than 2 mm per minute.

13. A single crystal obtained with the aid of the method claimed in any preceding claim.

14. A semiconductor device comprising a monocrystalline semiconductor body obtained from a single crystal as claimed in claim 13.

15. A photosensitive target comprising a monocrystalline semiconductor body obtained from a single crystal as claimed in claim 13.

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